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CHARACTERIZATION OF ETHER ELECTROLYTES FOR RECHARGEABLE LITHIUM CELLS

by

K. M. Abraham, J. L. Goldman and D. L. Natwig

Prepared for Publication
in the
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CHARACTERIZATION OF ETHER ELECTROLYTES FOR RECHARGEABLE LITHIUM CELLS

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ABSTRACT

2Methyl-tetrahydrofuran(2Me-THF)/$LiAsF_6$ and several diethyl ether (DEE)/$LiAsF_6$-based electrolytes have been characterized for their usefulness in rechargeable Li/TiS_2 cells. This characterization has involved extended room temperature cell cycling at various depths of discharge, evaluation of rate/capacity behavior of cells at 25°C and -10°C, and storage of cells at 50°C for up to one month with subsequent cycling. The thermal stability of the electrolytes at 71°C was evaluated by storage experiments in sealed-tubes, followed by product analysis. The performance of 2Me-THF/$LiAsF_6$ cells far surpassed the others. The present data further substantiate previous reports from this laboratory of the superior behavior of 2Me-THF/$LiAsF_6$ solutions in rechargeable Li cells. The DEE/$LiAsF_6$-based electrolytes are too unstable thermally to be practically useful.

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*Electrochemical Society Active Member.

Key Words: Lithium Cycling efficiency, electrolyte stability.

INTRODUCTION

Discoveries during the past few years of new organic electrolytes (1), together with advances in positive electrode technology (2) and cell fabrication capabilities (3,4) have made ambient temperature rechargeable Li cells a practical reality. Noteworthy among these advances are the identification of highly desirable electrolyte systems such as 2Me-THF/$LiAsF_6$ at EIC Laboratories (5,6) and 1,3-dioxolane/$LiClO_4$ by Exxon Corporation (7), and the construction and testing of Li/TiS_2 (4), Li/V_6O_{13} (3) and Li/MoS_3 (4) cells with nominal capacities ranging from 5-20 Ah. Because of a tendency to detonate upon impact, the 1,3-dioxolane/$LiClO_4$ system has been abandoned (8). The present electrolyte of choice for rechargeable Li cells is 2Me-THF/$LiAsF_6$ (1,3,9,10).

The Li electrode in Li/TiS_2 and Li/V_6O_{13} cells utilizing 2Me-THF/$LiAsF_6$ has typically cycled at charge densities of 7-10 mAh/cm^2 with a figure of merit, $F.O.M._{Li}$ of ~40. The $F.O.M._{Li}$ is given by the relationship (11).

$$F.O.M._{Li} = \frac{\text{total accumulated discharge capacity}}{\text{theoretical Li capacity}} \qquad (1)$$

While this cycling efficiency is very impressive, a $F.O.M._{Li}$ of 40 means that a cell requiring a life of 200 deep discharge cycles (100% depth of discharge, d.o.d.) would need a minimum of five times the Li capacity to that of the cathode. This amount of Li, although it leads only to a small reduction in the cell's specific energy, causes a significant reduction in its volumetric energy density (4). Another limitation of 2Me-THF/$LiAsF_6$, which is discussed in this paper, is the rather poor rate capability of its cells below 0°C. Clearly, electrolytes superior to 2Me-THF/$LiAsF_6$ are desirable for applications which require rechargeable Li cells with higher energy densities and better low temperature performance.

A promising class of electrolytes, recently discovered at EIC (12), has been those based on diethyl ether(DEE)/$LiAsF_6$. Studies in half-cells with DEE/$LiAsF_6$(2.5M) have shown that the Li electrode cycles with a $F.O.M._{Li} \geq 50$. In addition, it was found that the low conductivity, 1.2×10^{-3} $(\Omega cm)^{-1}$, of the DEE/$LiAsF_6$(2.5M) solution could be improved by "blending" the electrolyte, in 10-20 volume/percent (v/o), with ethers such as tetrahydrofuran (THF), 2Methyl-furan (2Me-F), 1,2-dimethoxyethane (DME) or 1,3-dioxolane (D). These blended electrolytes exhibited Li cycling efficiencies equal to or exceeding that in the parent solution despite of the poor Li cycling ability of the solvent additives to the ether. Although these half-cell cycling efficiencies represent the highest achieved to date in any organic electrolyte, they have been obtained at a rather low Li charge density of ~1 coul/cm^2.

In order to fully assess their practical utility, the DEE-based electrolytes have been evaluated in hermetic Li/TiS_2 cells. The results are presented here. The studies include evaluation of cycle life, Li cycling efficiency, rate/capacity behavior versus temperature and storage characteristics at 50°C of 0.68 Ah, Li/TiS_2 cells utilizing $(C_2H_5)_2O$/$LiAsF_6$ (2.5M) or its blends with THF (10 and 20 v/o), DME (10 v/o), D (10 v/o) or

2Me-F(10 v/o). The results are compared with those of cells containing 2Me-THF/$LiAsF_6$ (1.4M).

EXPERIMENTAL

General

All experiments were conducted in the absence of air and moisture under an Ar atmosphere in a Vacuum-Atmospheres Corporation dry box equipped with a Model He-493 Dri-Train.

Materials. Diethyl ether (DEE), tetrahydrofuran (THF), dimethoxyethane (DME) (Burdick and Jackson, distilled-in-glass) and lithium hexafluoroarsenate ($LiAsF_6$) (U.S. Steel Agri Chemicals, electrochemical grade) were used as-received. Lithium foil was obtained from Foote Mineral Company sealed under Ar. 2-Methyl tetrahydrofuran (2Me-THF), 2-Methyl furan (2Me-F) and 1,3-dioxolane (D) (Aldrich Chemical Company) were distilled off CaH_2 under Ar from a Perkin-Elmer Model 251 Auto Annular Still. The reflux ratio was 5:1 and the middle 70% fraction was collected. The distilled 2Me-THF typically had ~0.2% 2Me-F impurity, as evidenced by G. C. analysis.

The electrolytes, 2Me-THF/$LiAsF_6$(1.4M), DEE/$LiAsF_6$(2.5M) and the blended electrolytes, DEE(90 v/o):THF(10 v/o)/$LiAsF_6$(2.5M), DEE(80 v/o):THF(20 v/o)/$LiAsF_6$(2.5M), DEE(90 v/o):2Me-F(10 v/o)/$LiAsF_6$(2.5M), DEE(90 v/o):DME(10 v/o)/$LiAsF_6$(2.5M) and DEE(90 v/o):D(10 v/o)/$LiAsF_6$(2.5M) were prepared as described previously (3,5). The blended electrolytes are designated Blend 90-THF, Blend 80-THF, Blend 90-2MeF, Blend 90-DME and Blend 90-D respectively.

Li/TiS_2 Cells

Synthesis of TiS_2. TiS_2 was synthesized by a vapor transport technique by reacting Ti (sponge, Fisher Scientific Company) and S (powder, precipitated purified, Alfa-Ventron) at ~600°C. It was characterized by X-ray and chemical analyses. For the latter, the material was oxidized in air at ~700°C and weighed as TiO_2. The material used in the cells typically had the composition, $Ti_{1.02}S_2$.

Cathode Preparation. The cathodes were prepared as pressed powder electrodes. An intimate mixture consisting of 84 w/o TiS_2 (-80 mesh), 8 w/o C (Shawinigan 50% compressed) and 8 w/o Teflon was prepared in a blender. The mixture was pressed on either side of an expanded Ni screen (Exmet Corporation, 5Ni7-4/0) at a pressure of ~1000 lbs/in^2. The electrodes typically had a thickness of 1.125 mm. The cathode loading capacity typically was 17 mAh/cm^2.

Test Cells. Cells were all hermetically sealed. The electrode package comprised two cathodes and three Li anodes, arranged in an alternating fashion with Li forming the outer electrodes in the stack. Each cathode had an area of 10 cm^2/side so that the total cathode area was 40 cm^2. The total cathode capacity was 680 mAh ($1e^-/TiS_2$) or 17 mAh/cm^2. The Li electrode was fabricated from 10 mil Li foil. The middle electrode had two pieces of the Li foil (10 cm^2) on each side of the Ni screen and the outer electrode had one piece of Li (10 cm^2) on the side of the Ni screen facing the cathode. The total theoretical Li capacity typically was 1820 mAh (45.5 mAh/cm^2). Each Li electrode was bagged in two layers of Celgard

2400, polypropylene separator. The electrode package was introduced into a D-cell can (Ni plated cold-rolled steel) and compression was applied to the electrode package by Teflon hemi-cylinders. The cell was vacuum filled with ~12 ml electrolyte through a fill-tube on the cell cover assembly.

Cells were cycled galvanostatically with the aid of standard cycling equipment. The potential limits were 1.6V for discharge and 3V for charge. However, in most experiments cells were discharged to depths of 3, 7 or 10 mAh/cm^2 only so that the lower voltage limit was reached only towards the end of cell life. A cell was considered failed when its capacity decreased to less than 50% of the discharge capacity desired in a particular cycling regime. Any Li remaining on the anode was determined by electrostripping it by deep discharging the cell to ~-2V. The Li cycling efficiency, F.O.M.$_{Li}$, was calculated using the relationship given in Eq. 1. In obtaining the rate/capacity data, the cell was successively discharged at current densities between 0.5 and 8 mA/cm^2, with each discharge followed by a charge at 0.5 mA/cm^2. Data collection and retrieval were done with a Bascom-Turner 8000 Recorder equipped with microprocessor accessories.

Electrolyte Stability Experiments. Liquid samples were sealed in Pyrex glass tubes equipped with break-seals as described previously (13). After two weeks of heating at 71°C, the tubes, attached to a vacuum-line, were opened at the break seal and the gases were separated by vacuum distillation. UV-visible spectra of liquids were obtained on a Perkin-Elmer double beam spectrometer. IR spectra were obtained on a Beckman Aculab-5 Spectrometer. Liquid (0.025 mm path length) and gas (10 cm path length) cells were equipped with KBr windows.

RESULTS AND DISCUSSION

Some of the properties of the various electrolytes discussed in this paper including typical Li cycling efficiencies achieved in half cells are listed in Table 1. The low charge density Li cycling ability of the DEE-based electrolytes far exceeds that of 2Me-THF/$LiAsF_6$. It is also apparent that blending the DEE/$LiAsF_6$(2.5M) solution with 10 v/o of other ethers such as THF, DME, 2M-F or D results in an increase in both the conductivity of the solution and the cycling efficiency of the Li electrode. The highly regular and dendrite-free morphologies of the Li plates observed in blended DEE/$LiAsF_6$ solutions have been discussed previously (12). The higher conductivity exhibited by the blended electrolytes may be attributed to a more desirable complexation of Li^+-ions by the minor ether component. The noticeably higher cycling efficiency of the Li electrode in the blends than in the parent DEE/$LiAsF_6$(2.5M) may be, in part, due to the higher conductivities of the blended solutions.

While the half-cell Li cycling efficiencies achieved in the DEE-based electrolytes are far superior to any reported so far (1), the specific capacities of the Li plates have been extremely small. Practical (full) cells require Li plates with specific capacities exceeding 10 mAh/cm^2 (3,4,11). Moreover, the Li must cycle with high efficiencies at the high charge densities. The cycling efficiency of the Li electrode is determined by the properties of the electrolyte solution.

The electrolyte must be thermally stable in the long life-time of practical rechargeable Li cells. The electrolyte must also maintain fluidity with appreciable conductivity and Li^+-ion transport capability down to low temperatures (for example, -20°C) to be able to withstand with acceptable charge/discharge characteristics, the thermal excursions encountered by practical cells.

Li Cycling Efficiency in Li/TiS_2 Cells

The room temperature cycling efficiencies of the Li electrode in Li/TiS_2 cells have been measured as a function of the specific capacity of the Li plate. The results are given in Fig. 1. Typical galvanostatic charge/discharge cycles representative of the cycling regimes are depicted in Figs. 2-5. All experiments were carried out at least in duplicate and the reproducibility of the results was excellent.

Not only is the Li cycling efficiency in the 2Me-THF cells better than in DEE-based electrolytes, but also it is superior to that in 2Me-THF half-cells. While the cycling efficiency in 2Me-THF/$LiAsF_6$ is rather insensitive to the Li charge density, it shows a strong dependence in DEE-based electrolytes. Another trend which is apparent in the blended electrolytes is the strong effect of the ether additive on Li cycling. Clearly, the preferred electrolyte among the blends is Blend 90-THF.

The present data clearly indicate that the half cell data, representative of impractically low Li charge density cycling, do not have a real predictive value with respect to the usefulness of a given electrolyte in practical cells. To date we have seen a good agreement between half and full cell Li cycling efficiencies only with 2Me-THF/$LiAsF_6$. The Li/TiS_2 cells employed in this study were all identical and were constructed and handled under identical conditions. Therefore, it seems that the large discrepancy shown by DEE-based electrolytes - the large differences between half and full cell Li cycling efficiencies as well as the significant variations among the blends themselves - reflect solution characteristics not revealed in the very short (~1 day) half-cell tests. Some of the probable contributing factors are: (i) the thermal instability of the electrolyte which would be more aptly manifested in long-term cycle tests (1-2 months); (ii) a greater extent of reaction between Li and the electrolyte during the long term, high capacity cycle tests; (iii) significant differences in the morphology of the Li plates which can be caused by, (a) the environments of the half and full cells and (b) the lower electrolyte to Li ratio in full cells.

The results obtained with electrolyte storage experiments (vide infra) indicate that the thermal instability of the electrolytes may be a major cause of the lower cycling efficiencies in DEE-based cells. However, the involvement of other factors cannot be ruled out.

Koch et al. suggested (10) that DEE is effective in cycling Li in half-cells because it is reduced on Li to lithium ethoxide (LiOEt) which is insoluble and that this film may protect Li from further attack. These authors also suggested that LiOEt has the right Li^+ ion-transmission properties to allow Li plating. Presumably, in the blends the poorly Li cycling solvents such as THF, DME etc. are kept away by the LiOEt film. If we accept this hypothesis, we can see some basic differences between the Li surface characteristics of half and full cells. (The half-cells referred to are the types used in the studies in refs. (5) and (12)). The ideal ion-transmitting film visualized by Koch et al. may not be achieved in Li/TiS_2 cells. First of all, the electrode package in full cells is very tight. The dynamics of Li intercalation/deintercalation processes associated with the TiS_2 cathode (2) during cell cycling can impose significant pressure variations on the Li electrode surface. The film surface may have cracks or other inhomogeneities, permitting electrolyte migration and higher extents of Li-electrolyte reaction. Not only is a larger amount of Li isolated in each cycle, but the heightened reaction may also cause significant changes in Li plate morphology, eventually worsening the cycling efficiency. The significant differences observed in the performance of various blends may reflect the variations in the kinetics of the reaction between Li and the ether additive.

The insensitivity of Li cycling efficiency in 2Me-THF/$LiAsF_6$, either to Li charge density or to cell environments, may be indicative of a chemically different and/or a more flexible protective film (5,14). The exceptional behavior of the 2Me-THF system is further indicated by the data in Figs. 5 and 6 which compare the cycle life of two cells, one containing a theoretical 45.5 mAh/cm^2 and the other a 78 mAh/cm^2 Li electrode. Both electrodes exhibited nearly identical Li cycling efficiencies.

Cell Storage at 50°C

The relevant data are given in Table 2. Because of their poor Li cycling efficiencies, cells with DME or D blends were not evaluated.

The open-circuit-voltage (OCV) of none of the cell showed any change with time. Furthermore, the discharge capacity of cells after storage was practically identical to that typically obtained in their unstored analogs. These results manifest the overall compatibility between TiS_2 and the various electrolytes. The data also indicate that none of the electrolytes undergoes a gross degradation or reaction during storage.

The more significant data, however, are the Li cycling efficiencies. Identical cycling efficiencies have been obtained in both the stored and unstored 2Me-THF cells. The stored DEE-based cells show the following trends. The DEE-cell, exhibited (unlike fresh ones) a *significant* voltage delay at 1 mA/cm^2, but yielded (at 0.5 mA/cm^2) the same cycling efficiency as do fresh cells. The Blend 90-THF and Blend 80-THF cells, which exhibited little or no voltage delay even at 2 mA/cm^2, cycled with considerably reduced Li cycling efficiencies. The stored Blend 90-2MeF cell also cycled with a lower Li efficiency; but the decrease in efficiency caused by storage is less that observed in Blend-THF cells. These effects of cell storage on cycling may be ascribed to the solubilities of the protective film on the Li electrode. It appears that in DEE/$LiAsF_6$, the protective film, grows to a greater extent with storage, as indicated by the voltage delay, prevents significant reactions between Li and the electrolyte. Since LiOEt is apparently more soluble, especially at elevated temperatures, in polar solvents such as THF (12), it is possible that the protective film in the Blend-THF electrolytes during storage is subjected to a continuous dissolution-deposition process, permitting a continued attack of the Li by the electrolyte.

The above explanation not withstanding, the effects of storage may be related to the thermal stability of DEE-based electrolytes.

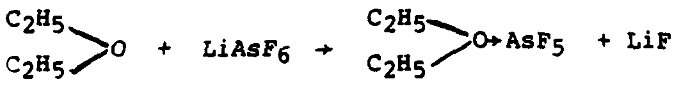
Thermal Stability of Electrolytes at 71°C

Electrolytes were stored with and without Li in evacuated sealed Pyrex tubes at 71°C. Some samples were also stored with all the components of a cell such as, electrolyte, TiS_2, C/Teflon mixture, Celgard 2400 separator and Ni screens.

Neither gassing nor any apparent decomposition was evident in any of the 2Me-THF/$LiAsF_6$ samples. However, their UV-visible spectra exhibited minor product peaks at 265, 285 (shoulder) and 330 nm. These products were found the least in samples containing all of the cell components. The excellent storage capability shown by the 2Me-THF cells suggests that whatever these minor storage products are, they are either not formed at 50°C or they do not affect Li cycling.

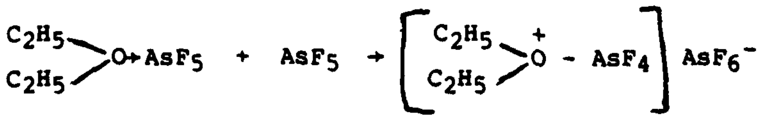
Unexpectedly rapid decomposition, i.e., in 2-3 days, occurred in DEE-based electrolytes. The decompositon of DEE/$LiAsF_6$(2.5M) or Blend 90-THF solutions occurred irrespective of whether the solutions contained Li or other cell components. However, the solvents themselves were stable. In all samples, $CH_2=CH_2$ was found by IR in the gas phase. When Li was present, H_2 was also found. (It should be noted Li/DEE samples did not produce H_2 in the absence of $LiAsF_6$). A major solution product was a pink oil which exhibited UV-visible absorption maxima at 450, 380 and 270 nm. The pink oil, which is soluble in electrolyte but only sparingly soluble in DEE itself, was isolated by repeated extraction with DEE. It showed IR absorptions characteristic of both C_2H_5 (1400, 1450-1480 cm^{-1}) and As-F (670-730 cm^{-1}) functionalities. However, it did not exhibit the characteristics C-O-C linkage absorptions at ($\sim$1125 cm^{-1}). Most probably it is a mixture of $C_2H_5AsF_6$ and $C_2H_5OAsF_4$. The isolated material decomposes in a few days at room temperature to form a glassy brown solid, which we believe is an [As-O-As] polymer (14).

We believe that the following sequence of reactions occur:

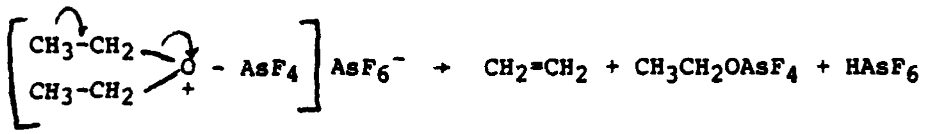


$$(C_2H_5)_2O + LiAsF_6 \rightarrow (C_2H_5)_2O\rightarrow AsF_5 + LiF \qquad (2)$$

Reaction 2 is supported by the fact that addition of AsF_5 to DEE and mild heating lead to identical products. This first step is probably followed by:



$$(C_2H_5)_2O\rightarrow AsF_5 + AsF_5 \rightarrow \left[(C_2H_5)_2\overset{+}{O} - AsF_4\right]AsF_6^- \qquad (3)$$



$$\left[\begin{matrix}CH_3\text{-}CH_2\\CH_3\text{-}CH_2\end{matrix}\overset{+}{O} - AsF_4\right]AsF_6^- \rightarrow CH_2{=}CH_2 + CH_3CH_2OAsF_4 + HAsF_6 \qquad (4)$$

$$\underset{\textstyle (I)}{2C_2H_5OAsF_4 \rightarrow C_2H_5F + C_2H_5OAsF_3\text{-}O\text{-}AsF_4} \qquad (5)$$

$$n\ I \twoheadrightarrow C_2H_5F + [As\text{-}O\text{-}As]\ \text{polymer} \quad (6)$$

$$C_2H_5F + AsF_5 \rightarrow C_2H_5AsF_6 \quad (7)$$

$$CH_2{=}CH_2 + HAsF_6 \rightarrow C_2H_5AsF_6 \quad (8)$$

$$HAsF_6 + Li \rightarrow 1/2H_2 + LiAsF_6 \quad (9)$$

Our experience is that with ethers such as THF, this type of reaction is suppressed by presence of Li. One main structural feature of DEE is that it contains groups which allow easy 1,2-elimination. It should be noted that the instability of ether/$LiAsF_6$ solutions at temperatures >100°C has been previously discussed by Koch et al. (15).

Rate/Capacity Behavior of Li/TiS_2 Cells

The relevant data, plotted as percent cathode utilization (based on $1e^-/TiS_2$) versus current density (mA/cm^2), for cells containing 2Me-THF/$LiAsF_6$(1.4M), DEE/$LiAsF_6$(2.5M) and Blend 90-THF are shown in Fig. 7. The discharge curves for the Blend 90-THF cell at various current densities at 25°C are given in Fig. 8. The room temperature rate/capacity behavior of the Blend 90-THF cell is practically identical to that of the 2Me-THF cell (16).

A capacity equivalent to $>0.8e^-/TiS_2$ is realized at current densities $\leq 2mA/cm^2$. The utilization at 4 mA/cm^2 is $0.68e^-/TiS_2$ for the Blend 90-THF cell and $0.55e^-/TiS_2$ for the 2Me-THF cell. The nearly identical cathode utilizations in the two cells probably reflect very similar electrolyte conductivities. As would be expected from its lower conductivity, the rate capability of DEE/$LiAsF_6$(2.5M) at 25°C is rather poor. In fact, the rate capability of the DEE cell at 25°C compares only with that of the

Blend 90-THF cell at -10°C. In contrast to the Blend 90-THF cell, however, the 2Me-THF cell had practically no capacity at -10°C, even at 0.5 mA/cm^2.

In general, all the electrolytes discussed in this paper provide low to moderate rate cells. The rather poor rate capability of the cells at -10°C are believed to be due to the lower solubilities of the $(DEE)_n \cdot LiAsF_6$ or the $(2Me\text{-}THF)_n \cdot LiAsF_6$ solvates, causing an increase in solution viscosity and a decrease in solution conductivity.

CONCLUSIONS

The ability of 2Me-THF/$LiAsF_6$ to cycle Li well with high charge utilizations in a practical cell has been further demonstrated. This electrolyte exhibited exceptionally high thermal stability at 71°C. Cells stored at 50°C for up to one month performed as well as fresh cells, indicating the high practicability of 2Me-THF/$LiAsF_6$. A major deficiency of the system, however, is its poor rate capabilities below 0°C.

Among the various DEE-based electrolytes evaluated, Blend 90-THF is the most desirable. The practicability of this electrolyte, however, is shadowed by its limited thermal stability.

The present study has also demonstrated that Li cycling efficiencies achieved with an electrolyte in half-cells at very low Li charge densities do not have general predictive value with respect to the practicability of electrolyte.

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TABLE 1

PROPERTIES OF ETHER ELECTROLYTES

		Li Cycling in Half Cells		
Electrolyte	Specific Conductivity $(ohm\text{-}cm)^{-1}$	Current Density (mA/cm^2)	Specific Capacity $(coul/cm^2)$	Cycling Efficiency[1] $(F.O.M._{Li})$
2Me-THF/$LiAsF_6$(1.4M)	3.8×10^{-3}	5	1.125	25
DEE/$LiAsF_6$(2.5M)	1.2×10^{-3}	5	1.125	45
DEE(90%):THF(10%)/ $LiAsF_6$(2.5M)	4.3×10^{-3}	5	1.125	50
DEE(80%):THF20%)/ $LiAsF_6$(2.5M)	4.7×10^{-3}	5	1.125	50
DEE(90%):DME(10%)/ $LiAsF_6$(2.5M)	4.7×10^{-3}	5	1.125	45
DEE(90%):2Me-Furan(10%)/ $LiAsF_6$(2.5M)	3×10^{-3}	5	1.125	66
DEE(90%):Dioxolane(10%)/ $LiAsF_6$(2.5M)	3.3×10^{-3}	5	1.125	52

[1] Average of several experiments. Half cell results in these electrolytes have been initially published by Koch et al., see Refs. 5 and 12.

TABLE 2

STORAGE TEST RESULTS OF Li/TiS_2 CELLS

Electrolyte	Days Stored at 50°C	OCV		Capacity (e^-/TiS_2) at 1 mA/cm^2		Li Cycling Efficiency (F.O.M.$_{Li}$) after Storage[1]
		Initial	Final	Typical Fresh Cell	After Storage	
2Me-THF/1.4M $LiAsF_6$	33	2.40	2.40	0.90	0.90	40
DEE/2.5M $LiAsF_6$	15	2.40	2.40	0.81[2]	0.80[2]	9
Blend 90-THF	30	2.40	2.40	0.90	0.89	11
Blend 80-THF	15	2.40	2.40	0.90	0.90	10
Blend 90-2Me-F	17	2.40	2.40	0.90	0.90	9

[1] Li charge density = 3 mAh/cm^2.

[2] Capacity at 0.5 mA/cm^2, severe voltage delay of the stored cell prevented capacity measurement at 1 mA/cm^2.

FIGURE CAPTIONS

Fig. 1. Li cycling efficiencies achieved in Li/TiS_2 cells versus Li charge density. The 2Me-THF solution is 1.4M in $LiAsF_6$. All other electrolytes are 2.5M in $LiAsF_6$.

Fig. 2. Typical cycling curves of a Li/Blend 90-THF/TiS_2 cell. Current density, 1 mA/cm^2. Li charge density, 3 mAh/cm^2. Theoretical Li, 45.5 mAh/cm^2.

Fig. 3. Typical cycling curves of a Li/Blend 90-THF/TiS_2 cell. Current density, 1.5 mA/cm^2. Li charge density, 10.5 mAh/cm^2. Theoretical Li, 45.5 mAh/cm^2.

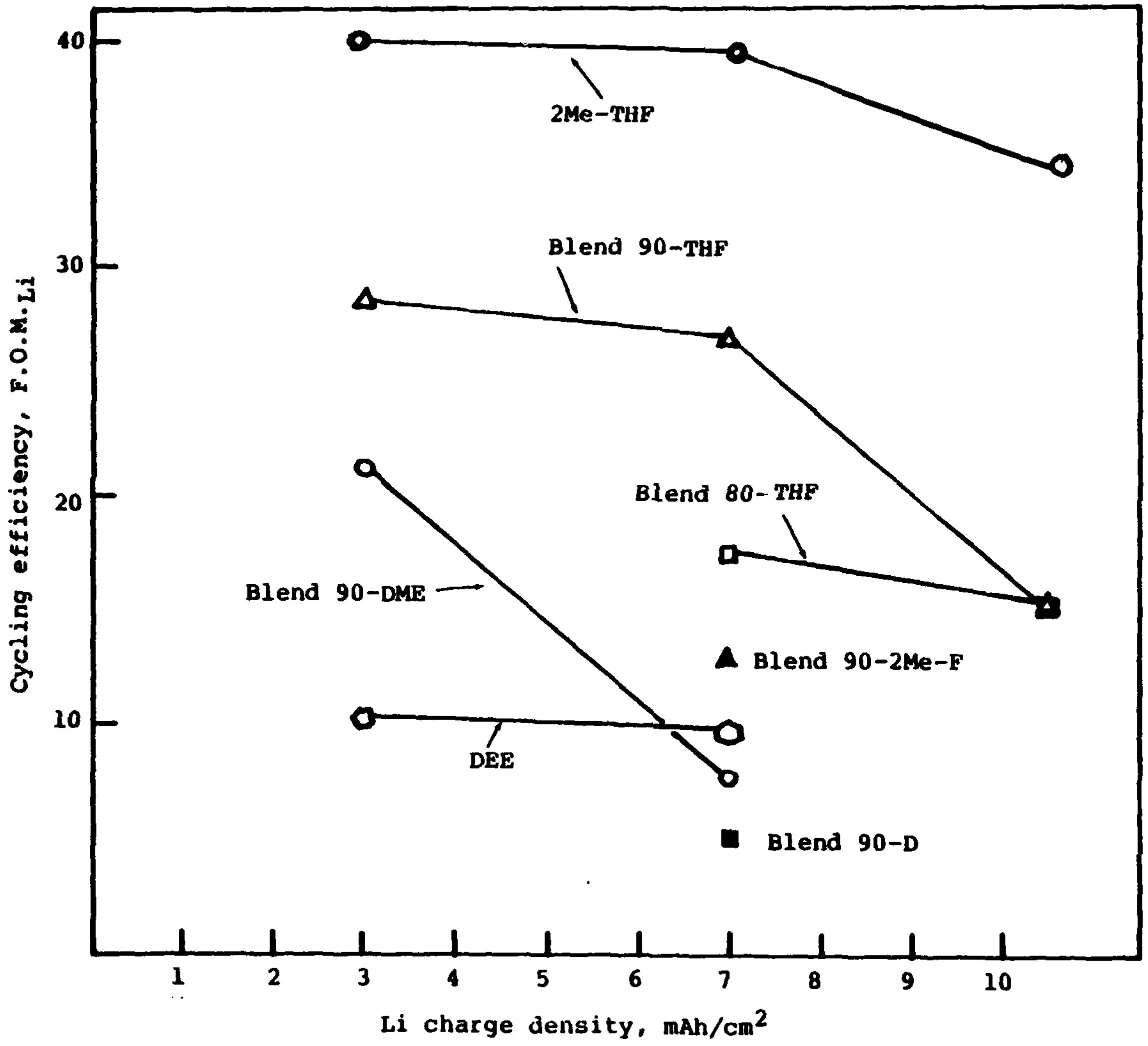
Fig. 4. Typical cycling curves of a Li/Blend 80-THF/TiS_2 cell. Current density, 1 mA/cm^2. Li charge density, 7 mAh/cm^2. Theoretical Li, 45.5 mAh/cm^2.

Fig. 5. Typical cycling curves of a Li/2Me-THF/TiS_2 cell. Current density, 1 mA/cm^2. Li charge density, 7 mAh/cm^2. Theoretical Li, 45.5 mAh/cm^2.

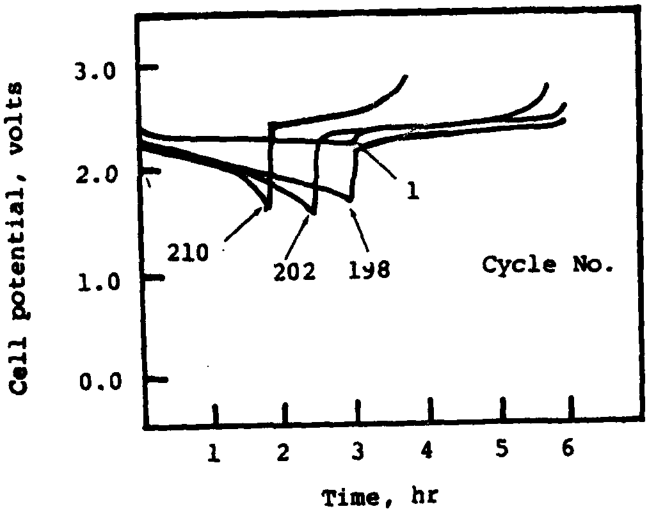
Fig. 6. Typical cycling curves of a Li/2Me-THF/TiS_2 cell. Current density, 1 mA/cm^2, Li charge density, 7 mAh/cm^2. Theoretical Li, 78 mAh/cm^2.

Fig. 7. Rate/capacity data for Li/TiS_2 cells.

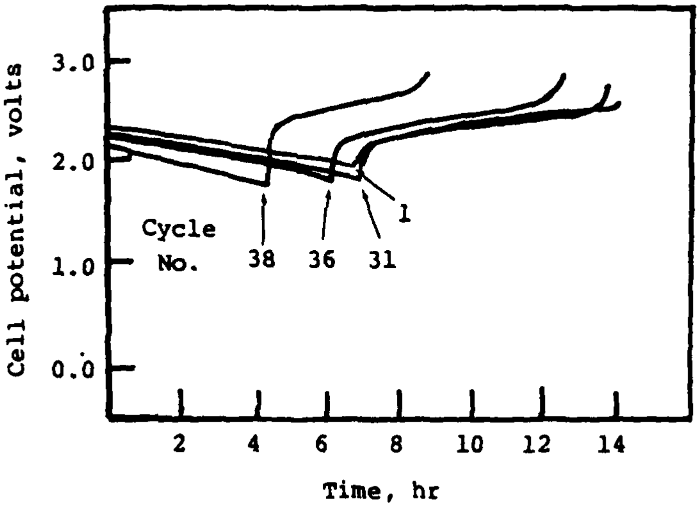
Fig. 8. Cathode utilization (based on $1e^-$/TiS_2) versus current density in a Li/Blend 90-THF/TiS_2 cell at 25°C.


40
30
20
10
Cycling efficiency, F.O.M.Li
1
2
3
4
5
6
7
8
9
10
Li charge density, mAh/cm2
2Me-THF
Blend 90-THF
Blend 80-THF
Blend 90-DME
DEE
▲ Blend 90-2Me-F
■ Blend 90-D

F1

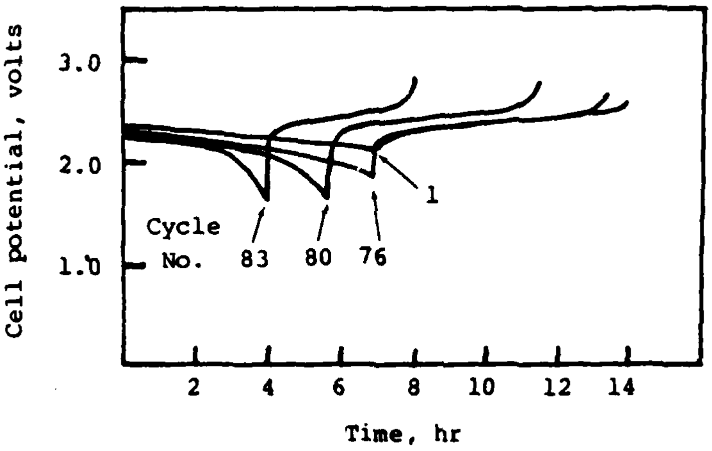

Cell potential, volts
3.0
2.0
1.0
0.0
1
2
3
4
5
6
Time, hr
1
210
202
198
Cycle No.

F2

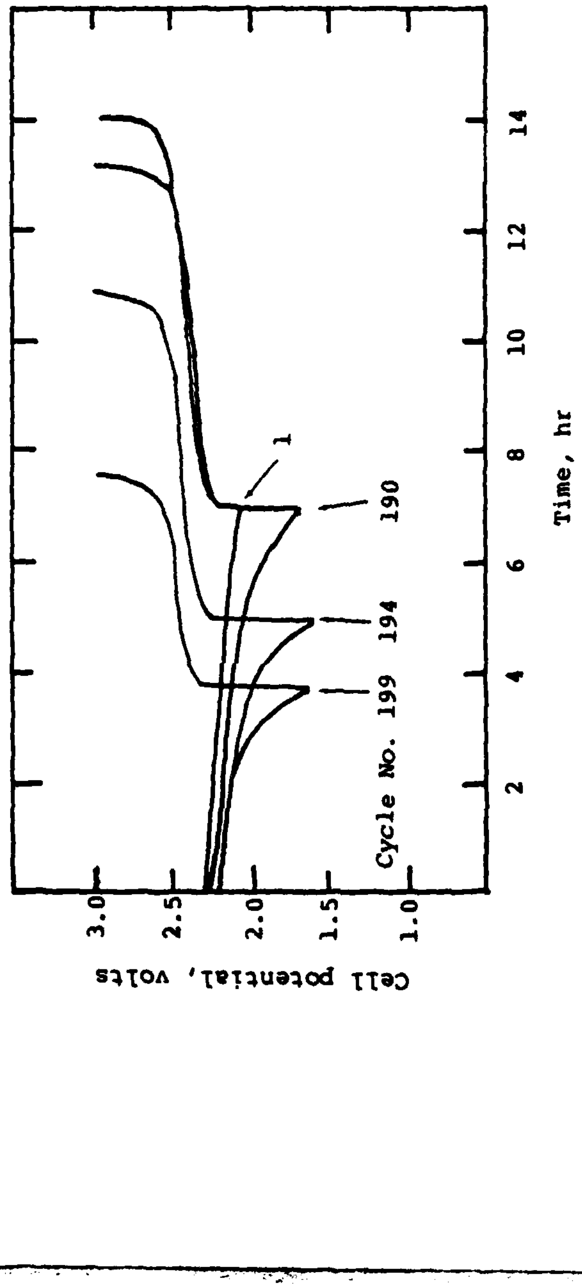


Cell potential, volts
3.0
2.0
1.0
0.0
Cycle
No.
38
36
31
1
2
4
6
8
10
12
14
Time, hr

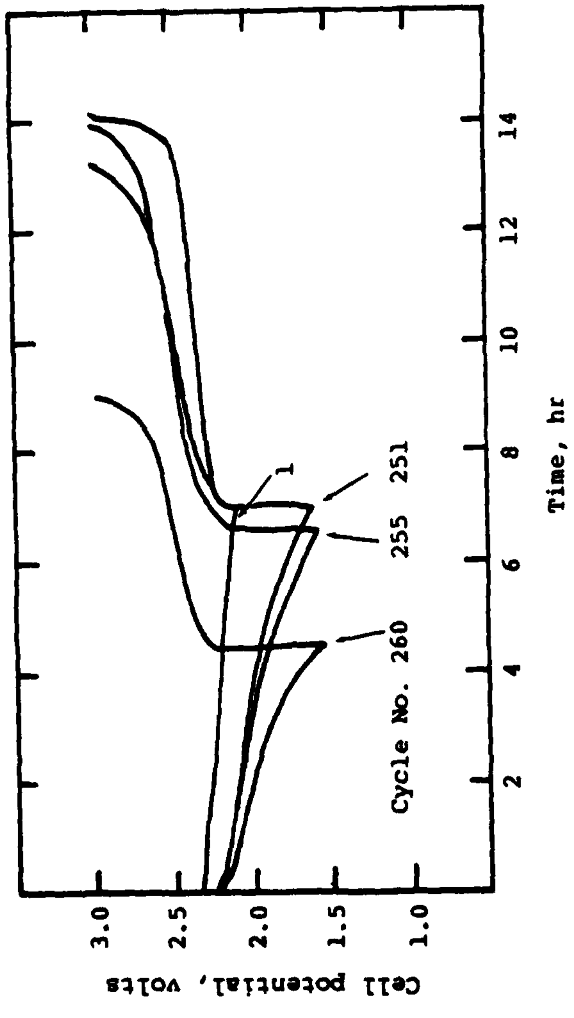
F3


Cell potential, volts
3.0
2.0
1.0
Cycle
No.
83
80
76
1
2
4
6
8
10
12
14
Time, hr

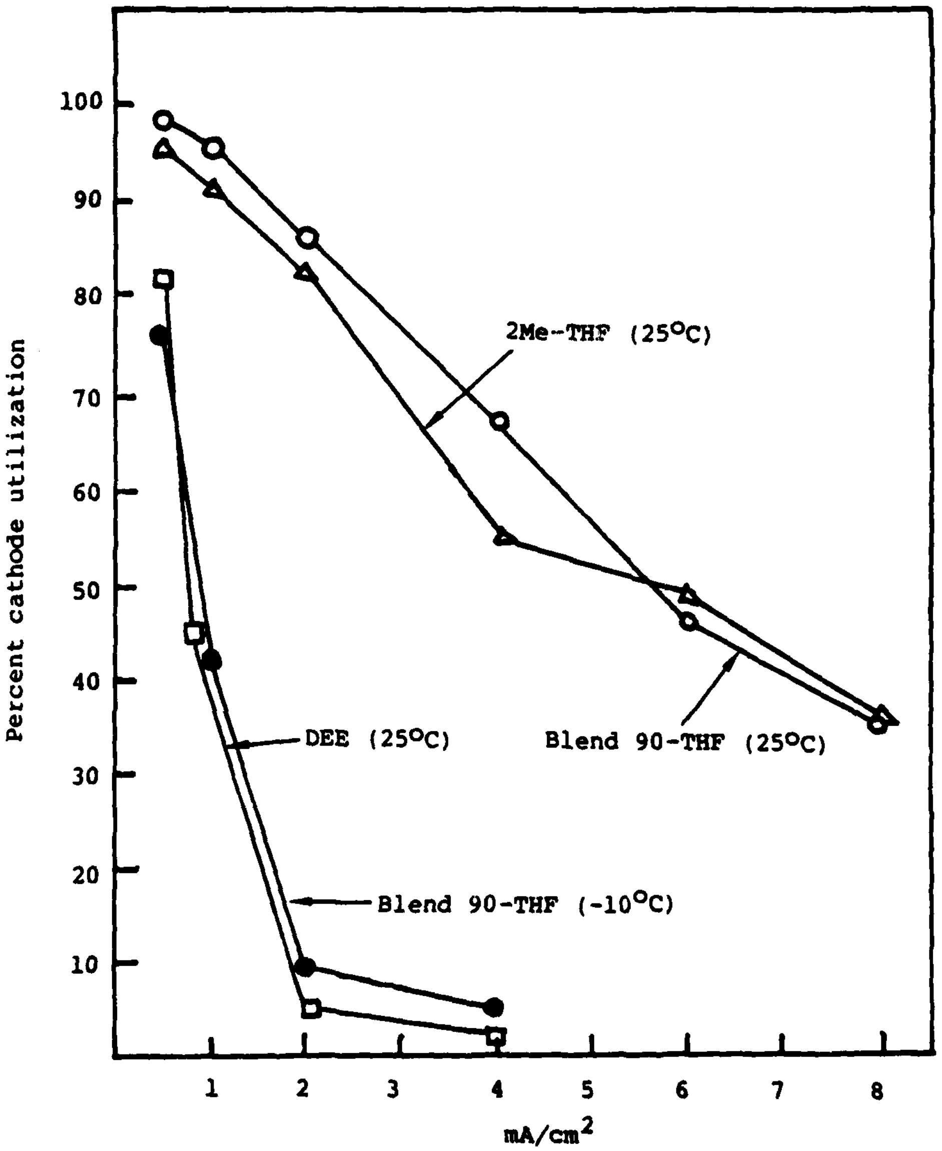
F 4


Cell potential, volts
3.0
2.5
2.0
1.5
1.0
Time, hr
2
4
6
8
10
12
14
Cycle No. 199
194
190
1

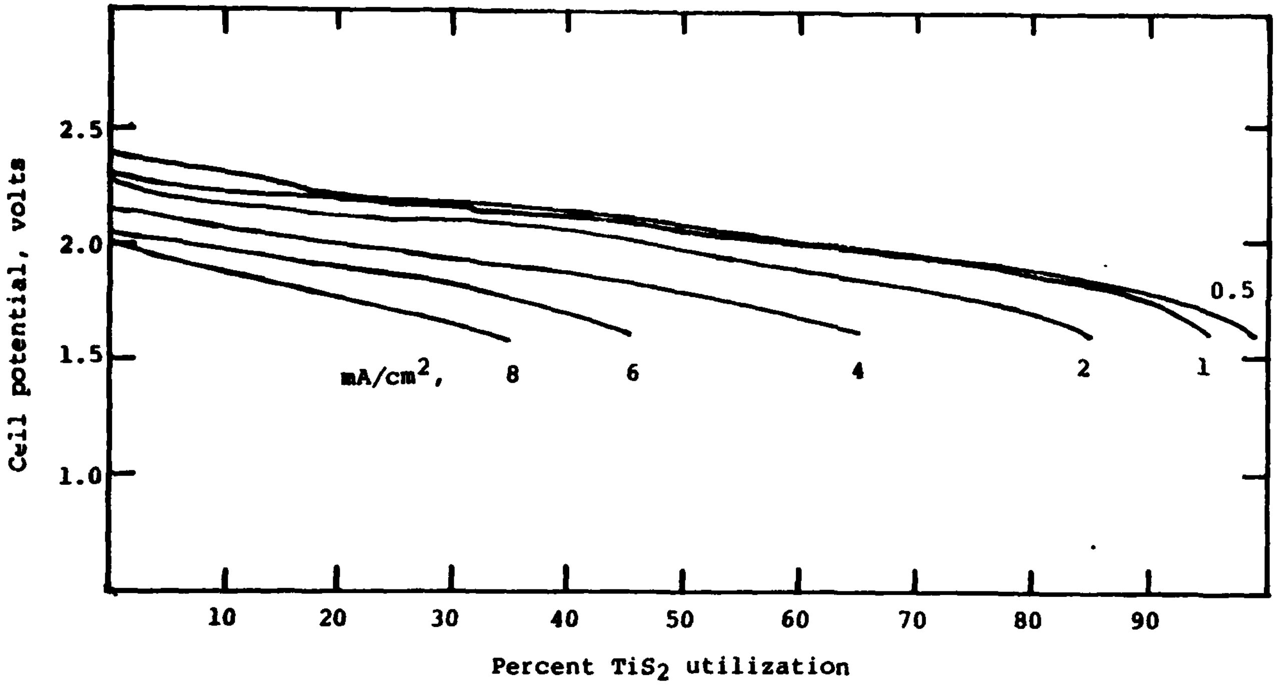
F5


Cell potential, volts
3.0
2.5
2.0
1.5
1.0
Time, hr
2
4
6
8
10
12
14
Cycle No. 260
255
251
1

F6


100
90
80
70
60
50
40
30
20
10
Percent cathode utilization
1
2
3
4
5
6
7
8
mA/cm²
2Me-THF (25°C)
DEE (25°C)
Blend 90-THF (25°C)
Blend 90-THF (-10°C)

F7


Cell potential, volts
2.5
2.0
1.5
1.0
10
20
30
40
50
60
70
80
90
Percent TiS$_2$ utilization
mA/cm^2,
8
6
4
2
1
0.5

F8

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